SCIENCE FOR CERAMIC PRODUCTION

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WALL CERAMICS FROM ZEOLITE-BEARING ARGILLACEOUS MATERIALS

A. G. Ashmarin[1] and A. S. Vlasov[1]

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The authors consider various aspects of expanding product range and increasing production volumes of wall ceramics. Physicochemical and technological properties of zeolite-bearing argillaceous materials are considered. It is shown using certain formulas and techniques it is possible to produce wall ceramics meeting contemporary construction requirements imposed on strength, cold resistance, and color range. It is observed that existing reserves of zeolite-bearing argillaceous materials make it possible to significantly expand the list of available minerals for coarse ceramics.

Ceramic brick has always been the preferred building material. Wall materials based on clay due to their physicomechanical properties, in particular, an equilibrium hygroscopic moisture create a healthy and comfortable ambient in buildings.

The simple and reliable construction technique and the relatively low cost are convincing arguments in favor of ceramic wall materials. One should also note a low maintenance cost and a long durability of brick structures (brick walls actually do not require complicated or expensive repair).

The share of ceramic brick in the total volume of building materials produced is high. Its production volume has stabilized in the past two years. In some regions a perceptible growth in brick production has been registered: 76 million pieces in the Central Region and nearly 20 million pieces in the Far East Region. Lately 14 factories with a total capacity of 344.3 million conventional bricks have been put into production [1]. Altogether 10 billion ceramic bricks have been produced in 2004.

The problems of available argillaceous materials is becoming urgent. The availability and accessibility of clays are important factors for the factories being constructed and for the existing facilities. Traditional materials for ceramics dwindle; less and less clay and loam can be used in the production of wall ceramics without correcting the compositions of ceramic mixtures. While reserves of high-quality argillaceous materials are depleted, the need to improve the product quality grows and the demand for ceramic facing bricks keeps increasing. Special attention is paid to brick color range and profiled shape, there is a demand for "antique-looking" materials and an increasing demand for large-size porous-hollow ceramic blocks with high heat-insulating properties: their thermal conductivity is 0.12 – 0.13 W/(m · K).

The purpose of the present study is to evaluate the possibility of expanding sources for ceramics production, in particular by using zeolite-bearing argillaceous rocks whose reserves are estimated as billions of tons. An identification attribute of such material is its "boiling up" under fast heating to the pyroplastic or melting state. Although this behavior is inherent in other hydrated aluminosilicates as well, zeolite has its unique microstructure with ports, channels, and cavities at the level of the crystalline lattice [2].

Since zeolite is capable of retaining large quantities of water in its structure, technological problems arise in production, for instance, in molding products under the standard absolute moisture of 20 – 25%. Products from zeolite-bearing clays can be molded on standard extrusion presses with an absolute moisture of 30 – 35%. This involves excessive energy consumption and complicates the process, as the molded product may become deformed under the effect of its own weight. At the same time, such materials are prone to swelling already at 1000 – 1050°C.

We tested two methods for producing wall ceramics: the traditional one and a second method, where a product is molded by extruding a mixture through a nozzle and where natural mineral additives (loam, tripolite, quartz sand) are added to the zeolite-bearing argillaceous mixtures.

[1] P. P. Budnikov VNIISTROM Institute, Moscow, Russia; D. I. Mendeleev Russian Chemical Engineering University, Moscow, Russia.

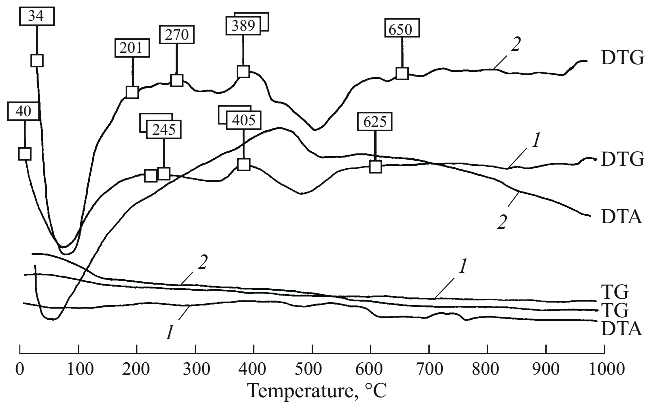

Fig. 1. Derivatograms of TsGS-1 (*1*) and TsGS-2 (*2*) samples.

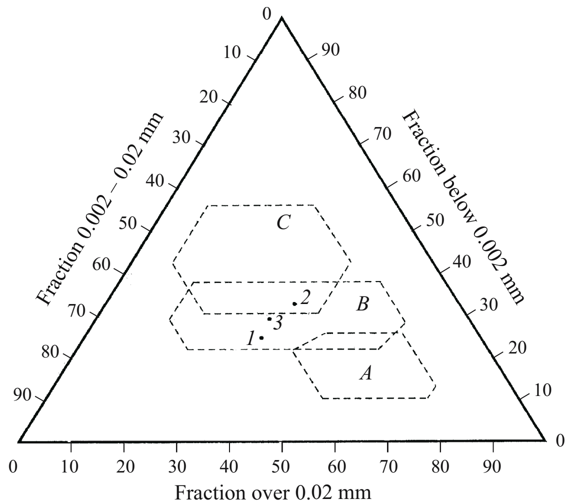

Fig. 2. Fraction diagrams of TsGS-1 (*1*), TsGS-2 (*2*) and tripolite (*3*) samples: *A*) standard brick; *B*) hollow brick; *C*) roof tile and highly hollow brick.

The essence of the second method is that while mixing a clay mixture, a certain amount of water depending on the structural-mechanical properties of clays is fed into the mixer: the amount of water could be up to 12% above the lower fluidity boundary (RF patent No. 2052418). Before the mixture was placed into a mold, a layer of a hygroscopic material was deposited on the inner mold surface. The preform was extracted from the mold after the surface layer reached a level of plastic strength ensuring a steady geometric size of the molded preform. This method in England is called "manual machine molding".

To study zeolite-bearing clays from the Kiprevskoe deposit (Vladimir Region) we used chemical, x-ray, petrography, and thermographic analysis, electronic and scanning electron microscopy, and other standard methods of analysis of ceramic mixtures.

At the first stage we determined the plasticity, drying sensitivity, air shrinkage, and physicomechanical properties of samples fired at 900, 950, 1000, and 1050°C, regardless of the molding method. It was found that as a content of zeolite in materials grows, their plasticity, drying sensitivity, and air shrinkage increase and the probability of swelling at about 1000°C increases as well. At the same time, the bending strength in samples fired at 1000°C grows from 15.9 to 20.1 MPa and compressive strength from 37.5 to 52.6 MPa.

On introducing from 10 to 30 wt.% quartz sand additive with the grain size modulus of 1.24, the strength of fired samples decrease 1.5 times, however, the introduction of 10% quartz sand totally prevents swelling of products in the temperature interval up to 1100°C. In this case the bending sand compressive strength insignificantly decreases (from 9.1 to 8.7 MPa and from 38.8 to 35.9 MPa, respectively). Tripolite can be introduced within a wide range of the clay : tripolite ratio. With their ratio of 50 : 50 the mixture becomes little sensitive to drying, sufficiently plastic, and well moldable for the product hollowness of 50%.

Thus, the polymineral zeolite-bearing argillaceous material can be used to produce high-quality wall ceramics, including porous-hollow stone (with hollowness up to 50%) with a low thermal conductivity.

We investigated zeolite-bearing materials whose mineral component contained from 15 to 28% zeolite. The additives preventing swelling and improving the molding and drying properties of mixtures were tripolite, quartz sand with the grain modulus of 1.74, and loam. The chemical and mineral compositions of zeolite-bearing materials and tripolite are given in Tables 1 and 2.

Differential thermal analysis indicated (Fig. 1) that when zeolite-bearing material is heated from 50 to 350°C, the majority of water (up to 85 wt.%) is removed. The fraction diagram of samples is shown in Fig. 2. On further heating from 350 to 750°C the removal of water continues, but the weight loss rate is significantly lower than in the initial period. In

TABLE 1

Material	Weight content, %, for absolutely dry sample										
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	P_2O_5	SO_3	calcination loss
TsGS-1	68.39	12.31	5.86	0.66	1.26	1.50	0.90	2.76	0.15	0.14	5.38
TsGS-2	66.53	13.14	4.58	0.87	1.35	1.73	0.91	2.60	0.14	0.78	6.79
Tripolite*	78.60	8.61	3.98	0.60	0.78	1.03	0.18	1.30	0.10	0.05	5.15

* The mineral component of tripolite contains around 42% opal-cristobalite phase.

TABLE 2

Material	Weight content, %						
	montmorillonite	hydromica	kaolinite	quartz	feldspar	zeolite	plagioclase
TsGS-1*	39.2	4.6	2.6	23.0 ± 4.0	10.0 ± 2.0	24.0 ± 4.0	–
TsGS-2	50.0	8.0	3.0	19.0 ± 4.0	–	15.0 ± 2.0	5.0 ± 1.0
Tripolite	34.0	8.0 ± 2.0	–	10.0 ± 2.0	3.0 ± 1.0	–	3.0 ± 1.0

* Besides, TsGS-1 sample contains 3.0 ± 1.0 pyrite.

this temperature interval zeolite becomes amorphous and the condensation of hydroxyl groups takes place. Furthermore, the transformation of minerals contained in the argillaceous materials takes place. One should especially distinguish the montmorillonite component of clay, whose content reaches up to 38%. Under slow heating it loses its capacity of swelling at high temperatures, which zeolite retains this capacity. Therefore, hydroxides in zeolite are retained longer than in argillaceous minerals. A more abrupt removal of hydroxides from clays under gradual heating causes their swelling at a temperature of 1100 – 1200°C [3].

Apart from three main crystalline phases (zeolite, quartz, and montmorillonite) the zeolite-bearing argillaceous material contains (%): up to 8 hydromica, up to 3 kaolinite, up to 20 quartz, up to 10 feldspar, up to 3 pyrite, up to 5 plagioclase. All these minerals affect the drying process and, particularly, the process of firing products.

Bricks were fired in an electric furnace of capacity 1 m^3 according to the following schedule: temperature rise from 100 to 700°C for 14 h, including an exposure for 3 h at 500°C; temperature rise from 700 to 950°C for 5 h and from 950 to 1050°C for 2 h. The exposure at the final firing temperature lasted 2 h, and cooling lasted 24 h.

The exothermic process in the temperature interval of 320 – 550°C is related to the condensation of hydroxyl groups. The phase transformation of the zeolite structure, which becomes amorphous, is registered in the temperature interval of 440 – 550°C. Furthermore, some processes are determined by the thermal transformations of impurity minerals.

The study performed suggests the following conclusions:

– zeolite-bearing argillaceous materials are suitable for the production of ceramic brick (resources of zeolite-bearing materials in Russia amount to around 3.5 billion tons);

– zeolite-bearing clays mainly have homogeneous chemical, granulometric, and mineral compositions;

– using zeolite-bearing materials in production does not require additional adjustment of the equipment;

– clays from the Kiprevskoe deposit have rather high color homogeneity across the entire bedding depth; depending on firing temperature their colors vary from pale pink to dark red;

– the product color range can be significantly expanded by introducing additives: from pale coffee to black.

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